Atomic Structures of Anomalous Carbon Dimers on the 3C-SiC(001)c(2x2) Surface

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INTRODUCTION

SiC has attracted much recent interests due to its potential for novel device applications as well as due to its unique surface structures/properties provided by the partly ionic character of Si-C bonding [1, 2]. Among the numerous polytypes, most of the current discussion on surface structures has been devoted to cubic 3C-SiC(001) [1] and hexagonal 6H(4H)-SiC(111) [2] surfaces. It has been known that the 3C-SiC(001) surface exhibits three major surface phases [1]: the carbon-terminated c(2x2) surface, the Si-terminated 2x1 (or c(4x2)) surface and the Si-rich 3x2 surface [3-6]. Although interesting and peculiar surface properties have been reported on these surfaces, further detailed discussion is mainly prohibited by the lack of consensus on the atomic structures of the surface reconstructions. As for the C-terminated c(2x2) surface, the possibility of a very unusual bridge-bonded dimer (BD) structure has been discussed (Fig. 1a) [7], which is unprecedented among the known semiconductor surface reconstructions, against a more conventional dimer structure (Fig. 1b) [8]. This structure seems to violate the most important rule of semiconductor surface reconstructions - minimization of the number of unsaturated dangling bonds. Extensive theoretical efforts have been devoted to find the ground state structure of the c(2x2) surface but to fail to get an unambiguous answer [9, 10]. Experimentally, a recent NEXAFS study provided an indirect evidence for the BD structure [11], which is, however, far from being conclusive.

In the present work, we unambiguously determined the quantitative details of the atomic structure of the 3C-SiC(001)c(2x2) surface by scanning-tunneling-microscopy (STM) and by photoelectron diffraction (PED) of the C 1s surface core level [12].

EXPERIMENTS

STM studies were done at Electrotechnical Laboratory (Tsukuba, Japan) and surface-core-level-resolved C 1s PED experiments on the beam line BL 9.3.2 of Advanced Light Source. Well-ordered single-domain 3C-SiC(001)c(2x2) surfaces were prepared by annealing 3C-SiC(001) films at ~ 1450 K (Si sublimation) *in situ* for the PED experiments [2, 4, 6]. In the STM study, the methods of Si sublimation and C_2H_2 or C_2H_4 exposure [2, 11] were extensively compared.

RESULTS AND DISCUSSION

Figures 1c and 1d show high-resolution filled-state STM topography of the c(2x2) surface. These images clearly show one oval-shaped protrusions in each c(2x2) unit cell for the first time, which is slightly elongated along the [110] azimuth (the C dimer bond axis of the BD model). These protrusions and their characteristic bias dependence appear uniformly over the whole surface. Extensive STM imagings of the surfaces prepared by C_2H_2 (C_2H_4) exposure and by Si

sublimation showed no essential difference. This result apparently denies any substantial coexistence of different c(2x2) or 2x1 surface reconstructions suggested by theories [9, 10]. However, due to the dramatic bias dependence of the STM images and its mismatch with the presently available calculations [9], the STM image alone can not point out the correct c(2x2) structure.

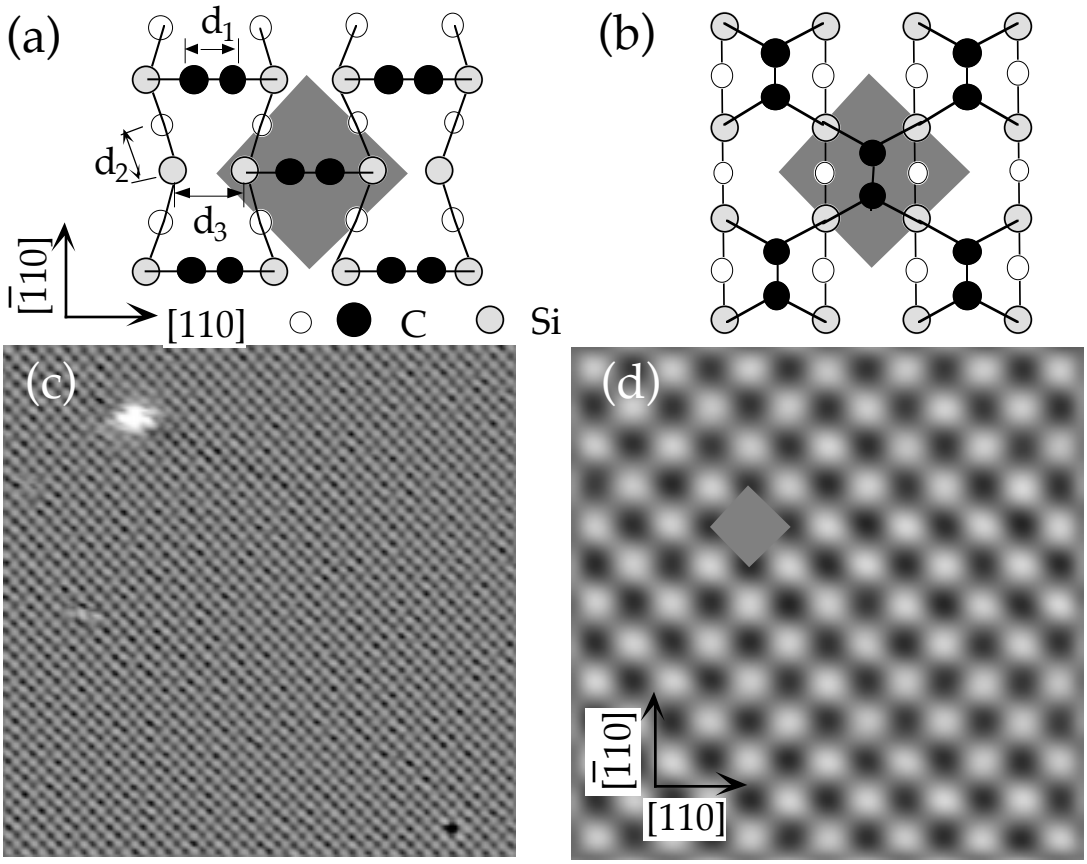

Fig. 1. The two structure models of 3C-SiC(001)c(2x2): (a) the bridge-dimer (BD) and (b) the staggered-dimer model (SD). Filled-state STM images of the 3C-SiC(001)c(2x2) surface: (c) a wide scan (195x195 Å) at a sample bias of -2.95 V and (d) a close-up (40x40 Å) scan at -3.05 V. A c(2x2) unit cell is depicted by hatched diamonds.

Further structural information can be achieved by resolving out the C 1s photoemission from the surface C atoms. Yeom et al.'s previous high-resolution C 1s study (done at Max-Lab BL-22) [6] have shown that the C 1s level is composed of two main components originating from the bulk C and the topmost C layers (**B** and **S**, respectively, in Fig. 2). The energy shift between **B** and **S** is as large as 1.1 eV indicating a large deviation of the electronic and structural environments of surface C atoms from those of bulk. However the fact that both SD and BD models have only single surface C sites prevents to distinguish them through the C 1s spectra. In order to obtain quantitative information on the surface structure, the PED from the surface C 1s component (**S**) was investigated [13, 14]. As shown in Figs. 2a and 2b, **S** shows a large intensity modulation when its kinetic energy ($hk^2/4\pi m_e$) is varied. This modulation, due mainly to the scattering of photoelectrons by the near-surface atoms, is measured in detail by scanning the photon energy and is, then theoretically simulated including the multiple scattering of photoelectrons fully with more-than-200-atom clusters of the two structure models. The optimized results of simulations through R-factor analyses [14] are compared to the experimental results in Fig. 2c. As evident in this

comparison, the SD model can be ruled out due to the apparent disagreement with the experiment. In sharp contrast, the BD model gives an excellent agreement between the experiment and simulation with a convincingly low R-factor of 0.11. The optimized structural parameters for the BD model are 1.22 ± 0.05 Å for the C-C dimer length (d_1), 1.84 ± 0.02 Å for the C-Si bond length between the top and the 2nd layers (d_2) and 2.70 ± 0.1 Å for the Si-Si bond length (d_3). This C-C bond length corresponds well to that of the triple-bonded C_2H_2 molecule and agrees very well with the theoretical calculations [9, 10]. This suggests the unique *triple bonding* of C dimers [9-11], which was further confirmed by Yeom et al.'s angle-resolved valence band photoemission study identifing two characteristic π-bond surface state bands as predicted by theory [12].

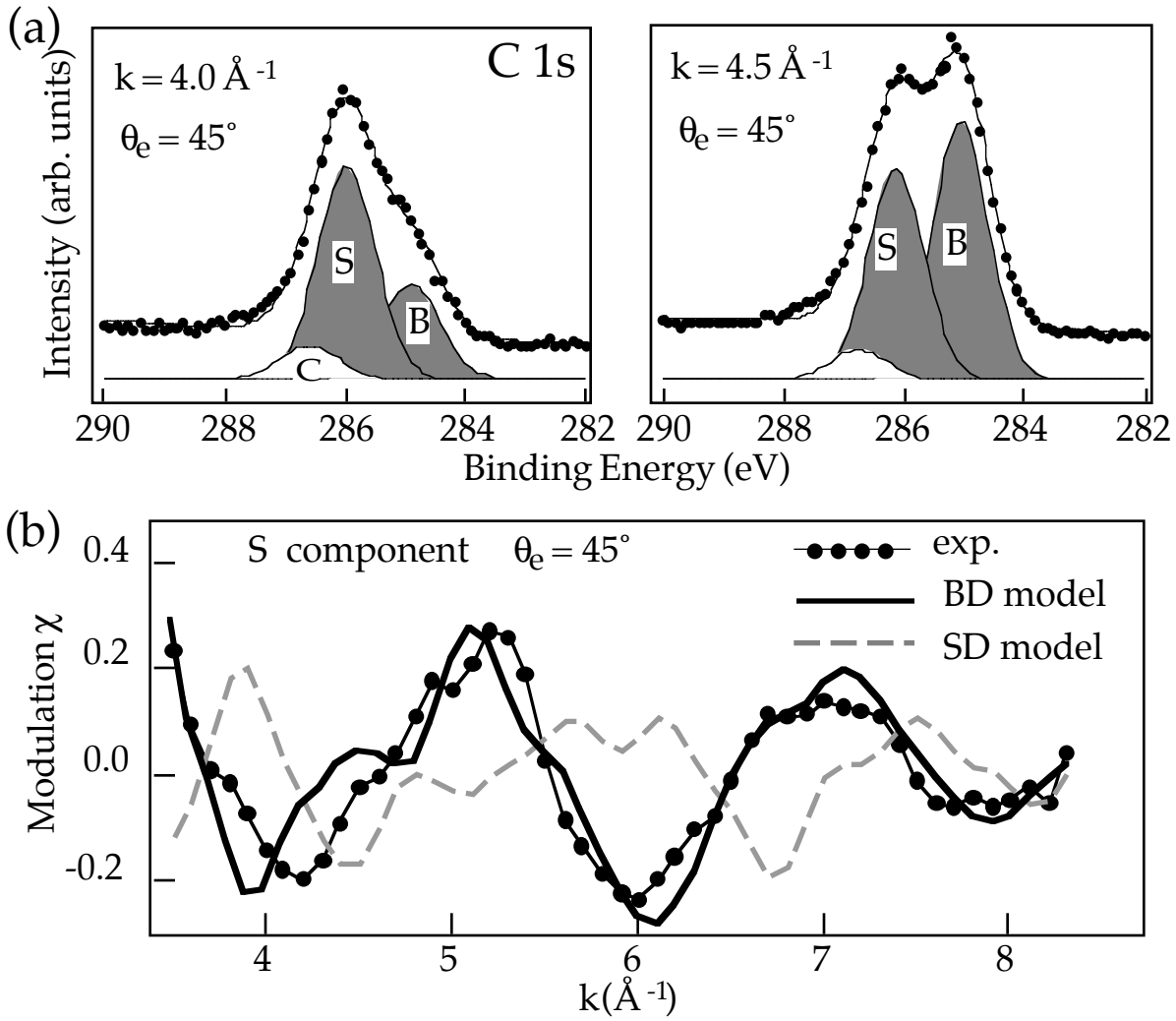

Fig. 2. (a) C 1s spectra of 3C-SiC(001)c(2x2) with decompositions taken along the [110] azimuth at an emission angle (θ_e) of 45° for the two different kinetic energies ($\hbar k_2/4\pi m_e$ where k = 4.0 and 4.5 Å^{-1}). S and B denote the surface and bulk components, respectively [6]. (b) Intensity modulation of the S component as function of photoelectron wave vector (k). This is given in the c function: $c = (I - I_0)/I_0$, where I is the photoelectron intensity and I_0 is its smooth background. The dots with a thin solid line represent the experimental data and the thick solid (dashed) line is the optimized result of theoretical simulations for the BD (SD) model.

CONCLUSIONS

The atomic structure of the c(2x2) reconstruction of the C-terminated 3C-SiC(001) surface was unambiguously determined by scanning tunneling microscopy and surface-core-level-resolved

photoelectron diffraction studies. This surface is found to uniformly consist of bridge-bonded C dimers with a C-C bond length of 1.22 Å. This indicates that the surface carbon atoms form unprecedenced *triple-bonded* dimers, which is further corroborated by detailed angle-resolved valence-band photoemission study identifing two occupied π -state bands due to the surface-normal and -parallel π orbitals of the triple-bonded C dimers [12].

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